RJC RASĀYAN JOURNAL OF CHEMISTRY Vol.1,No.1(2008),105-109

MICROWAVE ASSISTED SYNTHESIS, SPECTRAL AND ANTIBACTERIAL INVESTIGATIONS ON COMPLEXES OF Mn (II) WITH AMIDE CONTAINING LIGANDS

N. Bhojak* and Balvinder Singh
Green Chemistry Research Centre. P.G. Department of Chemistry,
Govt. Dungar College (A-Grade), University of Bikaner, Bikaner – 334003
E-mail: narendarbhojak@rediffmail.com

ABSTRACT

In this research work microwave technique have been utilized for the synthesis of free carboxylic group containing amide ligands and their complexes with Mn(II). The characterization of the compounds have been carried out on the basis of elemental analysis, infrared, electronic spectra and magnetic susceptibility studies. Antibacterial activity of the ligands and complexes have also been reported on S.aureus and E.coli microorganisms. The diffuse reflectance spectrums of the complexes show bands in the region 20,050 cm^{-1} to 26,3100 cm^{-1} assignable to $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_{1g}$ transitions. These are also typical of tetrahedral environment around the manganese. The magnetic moment (5.80 BM) of the complex indicates high spin tetrahedral environment. The microwave method of synthesis of complexes have been found easier, convenient and ecofriendly.

Keywords: *Microwave, amide, manganese (II).*

INTRODUCTION

Amides play vital roles in nature. All proteins are polyamides and make up a large part of the animals body[1]. They are found in all living cells and are principle materials of skin, muscles, nerves, blood, enzymes, antibodies and many harmones. Metal or metalloid amide are compounds which contain one or more $–CONH_2$ ligand groups or a simple derivative [such as –CONHR, $-CONR_2$, where R = methyl, phenyl, $SiMe_3$ etc.) attached to metal. Amides of sodium and potassium are the first examples of metal amides. Metal or metalloid amides may be mono, di-or poly nuclear and nitrogen is in a three coordinated environment. Metal amides include many important natural products such as heamin (a porphyrin), chlorophyll (a dihydroporphyrin), vitamin B12 etc. Importance of amide group containing compounds have also been recognized in various fields of chemistry and biology.[2,3]

Manganese is essential to organisms and activates numerous enzymes and for certain enzymes there appears to be a high specificity for manganese (II). Deficiency in soils has led to the infertility in mammals bone malformation in growing chicks.[4] Recently complexes of Mn(II) with high antimicrobial property have been reported and their characterization have been made on the basis of spectral investigations.[5,6]

The present research work describes the synthesis, spectral and antibacterial studies on the complexes of Mn (II) with amide group containing ligands. The complexes have been characterized on the basis of elemental analysis, infrared, electronic spectra and magnetic susceptibility studies.

EXPERIMENTAL

All the chemicals and solvents used were of AR grade. Purity of synthesized compounds has been checked by thin layer chromatography. IR spectra are recorded on FT-IR Perkin –Elmer spectrophotometer RX1 (νmax in cm^{-1}) using KBr disc. ^1H NMR spectra are recorded in $CDCl_3$

on a Bruker DRX-300 MHz using TMS as internal standard. The chemical shifts are reported as parts per million (ppm). Magnetic susceptibility measurements were carried out on the vibrating sample magnetometer (VSM) model 155 at 5500 Gauss field strength. Microwave synthesis was carried out in domestic microwave oven model L.G. MS-194W, 230-50Hz, 800W. Beck Man DU-64 Spectrophotometer, with quartz cell of 10mm light path was used for absorption measurement.

Synthesis of ligands by microwave irradiation : Four ligands i.e. N,N'-bis-(3-carboxy-1-oxopropanyl)-1,2-dimethylethylenediamine (CDMPE), N,N'-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-dimethylethylenediamine (CDMPE-2) N,N'-bis-(3-carboxy-1-oxopropanyl)-1,2-diethylethylenediamine (CDEPE), N,N'-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-diethylethylenediamine (CDEPE-2) were synthesized. In a typical preparation mixture of amine (1.0 mmol) and carboxylic acid (2.1 mmol) were taken in Erlen Meyer flask capped with a funnel placed in a microwave oven and irradiated at 200 watt for 2 minutes. The reaction was monitored by TLC. After completion the reaction, the reaction mixture was allowed to attain room temperature and solid separated was filtered. The crude product was recrystallized from redistilled ethanol.

Microwave Irradiation synthesis of Mn (II) complexes: For the preparation of various complexes, a slurry of ligand (i.e. CDMPE, CDMPE-2, CDEPE, CDEPE-2) (1 mmol) was prepared in water or in water-ethanol mixture. In this a solution of Mn $(CH_3COO)_2.4H_2O$ (1 mmol) was added. The resulting mixture was irradiated in a microwave oven for 2 to 6 minutes at medium power level (600W) maintaining the occasional shaking. The mixture was cooled to room temperature and poured into ice chilled methanol and dried in vacuum over P_2O_5. In order to synthesize complexes with CDEPE-2 prolonged irradiation and cooling was required.

Complexes and ligands were also synthesized by conventional method and results were found satisfactory.

RESULTS AND DISCUSSION

Ligands and complexes were identified on the basis of elemental analysis and spectral studies. Colour, yield and elemental analysis data are represented in Table 1.

Vibrational spectra: Few diagnostic ir bands are given in Table 2. $\nu_{(C=O)}$ and $\nu_{(C-O)}$ stretching frequencies in the region 1595-1535 cm^{-1} and 1420-1400 cm^{-1} observed for free ligands and assigned to asymmetric and symmetric modes respectively are shifted in the complexes. These shifts consequently increase the difference between the frequencies of asymmetric and symmetric modes of carboxylate group known as $\Delta\nu$. An increase in the value of $\Delta\nu$ has been ascribed to coordination of carboxylate groups to central metal ion in unidentate fashion. The ir bands due to amide $\nu_{(N-H)}$ mode observed at 3397-3209 cm^{-1} for the free ligands are shifted to higher frequencies indicating non-participation of N of amide group in coordination. Amide I bands due to $\nu_{(C=O)}$ shift negatively opposite to that of $\nu_{(N-H)}$ in the complexes suggesting carbonyl oxygen coordination. Bands observed at 257-224 cm^{-1} assigned to $\nu_{(Mn-O)}$[7-9]

Magnetic moments and electronic spectra: Room temperature magnetic moments of the Mn (II) complexes fall in the range 5.6 - 6.02 BM. These values are typical of tetrahedrally coordinated Mn which has five unpaired electrons. The visible spectra of these complexes have been measured in methanol are reported in Table 3. The observed values exhibits bands in the region 20,000 cm^{-1} to 26,000 cm^{-1} assignable to $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_{1g}, {}^4A_{1g}$ transitions. These are also typical of tetrahedral environment around the manganese[10-11].

Antibacterial activity: The antibacterial activity of the compounds against *E.coli* and *S.aureus* were carried out using Muller Hinton Agar media (Hi media). The activity was carried out using

paper disc method represented in Table 4. Among the various compounds CPPP and its Mn (II) complexes has been found out to be most effective against these microbes showing maximum clarity of zones.

CONCLUSIONS

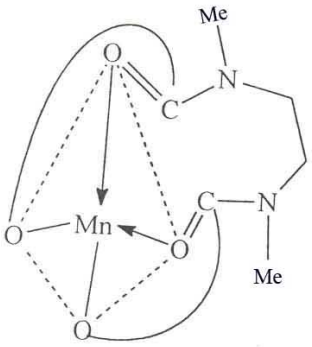
Mn (II) complexes were found to coordinate through amide oxygen and carboxylate oxygens as revealed by the i.r. spectroscopy. The magnetic moment for all the complexes recorded corresponds to five unpaired electron. Although we were unable to get single crystals for X-ray studies, magnetic, electronic and vibrational spectroscopic data showed the tetrahedral geometry for all the complexes. Tentative structure of complexes is proposed as Fig **1a** Mn(II)-CDMPE, **1b** Mn(II)-CDMPE-2, **1c** Mn(II)-CDEPE, **1d** Mn(II)-CDEPE-2.

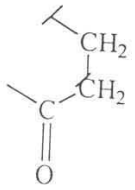
REFERENCES

1. V.L. Pecoraro, Li X. Baker, M.J. Butler and J.A. Bonadies, *Recueil Trav. Chim.*, ***106,*** 221 (1987).
2. B.S. Garg , N. Bhojak, R.K. Sharma, J.S. Bist and S. Mittal, *Talanta,* **48**, 49 (1999).
3. B. S. Garg , N. Bhojak, D. Nandan, *Ind. J. Chem*., **, 44A**, 1504 (2005).
4. G.C. Gotzias, *Fed. Proc. Supplement*, **10**, 98 (1961).
5. P.F. Rapheal, E. Manoj and M.R. Prathapachandra Kurup, *Polyhedron*, **26(17),** 5088 (2007).
6. B. S. Creaven, Denise A. Egan, Dariusz Karcz, Kevin Kavanagh, Malachy McCann, Mary Mahon, Andy Noble, Bhumika Thati and Maureen Walsh, *J. Inorg. Biochem*., **101 (8),** 1108 (2007).
7. S.D. Beukeleer, H.O. Desseyn, E.M. Zoupa and S.P. Perleps, *Trans. Met.Chem*., **19**,468 (1994).
8. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience Publication, p. 3 (1977).
9. R. Singh, K. Sharma and N. Fahmi, *Trans. Met.Chem*., **24**, 562 (1999).
10. R.C. Paul, R.S. Chopra, R.K. Bhambri and G. Singh, *J. Inorg. Nucl. Chem*.,**36**, 3703(1974).

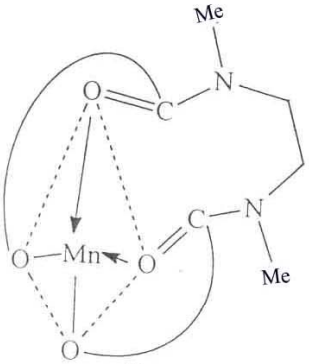
Table-1: Physico-Chemical Data of Mn (II) complexes (C.M. = conventional method; M.M. = Microwave method)

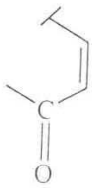
S.N.	Complex	Colour	Reaction Period		Yield %		Elemental Analysis Calcd(Found) %		
			C.M. h	M.M. min	C.M.	M.M.	C	H	N
1	Mn(II)-CDMPE	Off white	4	1.5	40	65	42.2 (40.4)	5.2 (5.5)	8.2 (7.9)
2	Mn(II)-CDMPE-2	Brown	5	2	30	50	42.4 (41.1)	4.7 (5.1)	8.2 (7.8)
3	Mn(II)-CDEPE	Brown	4	3	20	25	45.5 (44.4)	5.9 (6.2)	7.6 (7.9)
4	Mn(II)-CDEPE-2	Brown	5	5.5	30	55	45.7 (45.2)	5.4 (5.9)	7.6 (7.7)



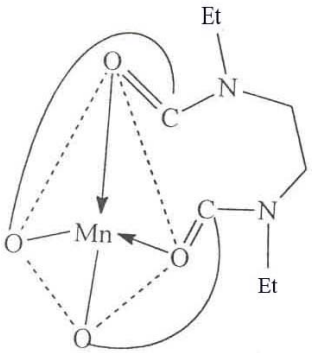
where) = 

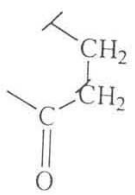
1a



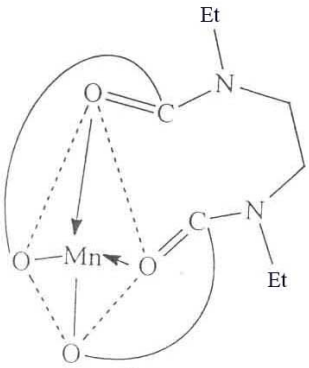
where) = 

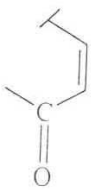
1b



where) = 

1c



where) = 

1d

Fig. Tentative structure of complexes

Table 2. IR Spectral assignments of diagnostic bands of ligand and its Mn (II) complexes

S.N.	Ligand and complexes	ν_{N-H}	$\nu_{C=O}$[a]	(ν_{C-N} $+\delta_{N-H}$)[b]	(ν_{N-H} $+\delta_{C-N}$)[c]	ν_{COO^-} (asym)	ν_{COO^-} (sym)	(ν_{Mn-O})
1.	CDMPE	3300	1643	1428	1280	1587	1419	---
2.	Mn(II)-CDME	3329	1610	1433	1310	1596	1421	240
3.	CDMPE-2	3387	1646	1461	1299	1580	1419	---
4.	Mn(II)-CDMPE-2	3390	1606	1479	1315	1594	1416	255
5.	CDEPE	3395	1635	1475	1301	1595	1400	---
6.	Mn(II)-CDEPE	3415	1619	1508	1312	1570	1331	244
7.	CDEPE-2	3220	1636	1480	1280	1535	1415	---
8.	Mn(II)-CDEPE-2	3310	1621	1493	1288	1541	1400	240

a = amide I band b = amide II band c = amide III band

Table 3. Magnetic moments and electronic spectral data of the Mn(II) complexes.

S.No.	Complex	μ_{eff} (BM)	Electronic Spectral bands $\lambda max(cm^{-1})$	Tentative assignments	Comment
1.	Mn(II)-CDMPE	5.58	26100 20280	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ $^6A_{1g} \rightarrow {}^4T_{2g}$	Tetrahedral Mn(II)
2.	Mn (II)-CDMPE-2	5.64	26310 20050	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ $^6A_{1g} \rightarrow {}^4T_{2g}$	Tetrahedral Mn(II)
3.	Mn (II)- CDEPE	5.70	26220 20275	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ $^6A_{1g} \rightarrow {}^4T_{2g}$	Tetrahedral Mn(II)
4.	Mn (II)-CDEPE-2	6.00	26218 20100	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ $^6A1g \rightarrow {}^4T_{2g}$	Tetrahedral Mn(II)

Table 4. Antibacterial activity of synthesized compounds

S.N.	Compound (100 ppm)	*E.coli*	*S.aureus*
1	CDMPE	8	10
2	Mn(II)-CDMPE	10	14
3	CDMPE-2	6	30
4	Mn(II)- CDMPE-2	7	28
5	CDEPE	2	30
6	Mn(II)-CDEPE-2	4	32
7	CDEPE-2	2	10
8	Mn(II)- CDEPE-2	5	10
9	Chloramphenicol	22	20

(Received: 29October 2007 Accepted: 5January 2008 RJC-146)